Microstructural dependence of vacancy diffusion in ordered alloys

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The dependence of the vacancy diffusional correlation factor on microstructure was investigated by Monte Carlo simulations (MCS). The MCS used activated state rate theory to model the vacancy diffusion. We varied the temperature, size of ordered domains, and the state of order within the domains. Correlations in the vacancy movement were found to vary widely, and numerical values are presented. Two different results were obtained, one for ordering in a homogeneous alloy and another for ordering in an alloy having domains. However, given the existence of domains, the vacancy correlation factor was observed to be independent of domain size. Oscillations in the correlation function were observed, and were attributed to pair trapping of the vacancy.

I. INTRODUCTION

Since correlated motions of atoms and vacancies occur during solid state diffusion, the Einstein expression for the diffusion constant, D, is modified by a multiplying a correlation factor, f.[1] For tracer atom diffusion via vacancies in an elemental metal, values of f such as 0.333, 0.467, 0.500, 0.653, 0.727, and 0.782 for the hexagonal, square, diamond, simple cubic, bcc, and fcc lattices were obtained many years ago.[2] For alloy diffusion, however, diffusional correlations are more complicated. A new feature arises in alloys—the vacancy itself no longer undergoes a random walk. The different species of atoms in an alloy usually have different atom-vacancy exchange frequencies. The atom with the highest jump frequency will tend to monopolize the vacancy, and the vacancy will tend to alternate between the sites occupied by this atom.[3] Interatomic interactions can cause local trapping of the vacancy; for example, vacancies are strongly trapped by domain boundaries.[4] Correlations in the vacancy movement are especially strong in alloys that develop long-range chemical order.

To date there have been several calculations of diffusional correlation factors for ordered alloys. The path probability method (PPM) was used by Kikuchi and Sato[5–7] to calculate correlation factors, but there were substantial disagreements with Manning's results based on random walk theory.[8,9] Much of this discrepancy can be alleviated with a time conversion procedure suggested by Sato and Kikuchi[10] and Sato.[11] Manning's random walk theory was extended to the case of ordered alloys by Bakker *et al.*[12–14] and Stolwijk *et al.*[15,16] These calculations provided reasonable agreement with correlation factors calculated by the Monte Carlo method.[17,18] A common feature of all these calculations is that they assumed the alloy was in a state of thermodynamic equilibrium. In a strict mathematical sense, the assumption of equilibrium is necessary in order to define a correlation factor. In practice, however, it is possible to define a correlation factor by observing a large number of jumps of vacancies or atoms in nonequilibrium systems. If during the time of observation the memory of the initial jump is lost and the state of the alloy has not changed significantly, a correlation factor has practical usefulness. Only a little effort has been made to study correlation factors in nonequilibrium alloys, however. In one such study[19] it was inferred that the correlation factor for vacancy diffusion was strongly suppressed at low temperatures. This suppression was beyond what could be obtained from pair approximation calculations, and occurred as the vacancy became trapped in local environments from which it had but a small probability for escape.[4,20–22] Many jumps of a vacancy are required for there to be a substantial change in the structure of the alloy, but this is not so for most tracer atoms. Therefore, in the present work it was impractical to obtain correlation factors for tracer atom diffusion.

In the present Monte Carlo simulations we varied the temperature, state of order, and antiphase domain boundary structure of an equiatomic binary alloy on a two-dimensional (2-D) square lattice, and we measured the vacancy diffusional correlation factor. Since the equilibrium state of order is a function of temperature, by varying these parameters independently we were often studying alloys removed from equilibrium. We found that the correlation factor decreased with increasing order within the domains and the correlation factor was independent of the domain size. The correlation factor was reduced markedly, however, when the alloy was homogenously ordered with no domains present. We obtained correlation factors ranging from near unity to as low as 0.01.

II. DIFFUSION MODEL

Consider a vacancy surrounded by z near-neighbor atoms. The probabilities of the vacancy-atom exchanges with the neighboring sites are

$$p_i=\frac{w_i}{\sum_{i=1}^{z} w_i}, \tag{1}$$

where w_i is the transition rate for the ith jump direction. The average time for a vacancy-atom exchange is

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$$\delta t=\frac{1}{\sum_{i=1}^{z} w_i}. \tag{2}$$

Using activated state rate theory the transition rate is

$$w=\nu e^{-\Delta E/k_b T}, \tag{3}$$

where ν is the attempt frequency, ΔE is the activation energy, and T is the temperature. Here ΔE is obtained using a broken-bond model. Let E_i be the energy required to break the chemical bonds between the diffusing atom and its neighbors, and E^* be the saddle point energy of the activation barrier. The activation energy is

$$\Delta E=E^*-E_i. \tag{4}$$

Recently we modified this approach to take into account the vacancy-solute interactions by adding an additional term to Eq. (4).[23] This term includes the vacancy-solute interaction energies for the initial and final states of the vacancy, e_i and e_f, which alter both the initial state energy and the saddle point energy. We assume that the initial state energy is $E_i+e_i+E_0$ and the saddle point energy is $E^*+(1/2)(e_f+e_i)+E_0$, where E_0 is the chemical energy due to all the atoms except the diffusing atom. The $(1/2)(e_f+e_i)$ term is used because when the diffusing atom is at the saddle point position, the vacancy is divided between two sites. The difference between the total initial state energy and saddle point energy is:

$$\Delta E=(E^*-E_i)+\tfrac{1}{2}(e_f-e_i). \tag{5}$$

Equations (1)–(5) define our Monte Carlo algorithm. To implement this algorithm on a digital computer we assume that the attempt frequency ν and saddle point energy E^* depend only on the identity of the diffusing atom. We also assume that the chemical energy E_i and solute-vacancy energies e_f and e_i result from pairwise near-neighbor bonding interactions where the species in the pair are denoted by a double subscript. Hence, for a binary alloy the physical parameters are (ν_A,ν_B), (E_A^*,E_B^*), (V_{AA},V_{AB},V_{BB}), and (V_{VA},V_{VB}).

We created alloy microstructures on a two-dimensional square lattice (128×128) with periodic boundary conditions. Only one site was occupied by a vacancy. Binary equiatomic microstructures were created using a random seed method in which a finite number of seeds were distributed randomly over the lattice. The seeds grew outward until they met. This provided the domain structure, after which the domains were filled with solute atoms using the formula

$$p(r)=\frac{1}{2}\pm\frac{1}{2}\eta\cos\left[\frac{2\pi}{a}(x+y)\right] \tag{6}$$

where $p(r)$ is the occupational probability at the site r. Equation (6) generates a checker-board pattern. Each domain was assigned a domain type at random [i.e., $\pm$ in Eq. (6)] in such a way that there were an equal number of the two domain types. We found that the random seed method produced microstructures that were very similar to those produced by Monte Carlo simulations of disorder to order transformations.[4]

Each random seed microstructure was the initial configuration for a Monte Carlo simulation that was run for one jump per atom. The parameters were $(\nu_A=\nu_B=1)$, $(E_A^*=E_B^*)$, and $(V=V_{AA}=V_{BB})$. Vacancy-solute interactions were set to zero $(V_{VA}=V_{VB}=0)$ for most runs. We varied the temperature, intradomain order parameter, and number of domains. Statistics of the vacancy motion were recorded and the autocorrelation functions and vacancy diffusional correlation factors were computed as described below. The data presented here on the autocorrelation function and the vacancy diffusional correlation factor are ensemble averages. These averages were performed over eight microstructures, although we also obtained averages for 16 and 32 microstructures for comparison.

III. VACANCY CORRELATION FACTOR

The vacancy diffusion coefficient can be computed from the results of a Monte Carlo simulation using the relation

$$D=\frac{l^2\Gamma f}{2d}, \tag{7}$$

where the l is the vacancy jump distance, Γ is the jump frequency, d is the spatial dimension, and f is the limit as $n\to\infty$ of the diffusional correlation factor

$$f_n=\frac{\overline{|\mathbf{R}_n|^2}}{l^2 n}. \tag{8}$$

The quantity $\overline{|\mathbf{R}_n|^2}$ is the mean-squared distance that a vacancy travels in n jumps.

Let $\{\delta\mathbf{r}_i,\delta t_i\}$ be a sequence of displacement vectors and transition times for a finite number of vacancy-atom exchanges. The jump frequency is

$$\Gamma=1/\overline{\delta t}, \tag{9}$$

where

$$\overline{\delta t}=\frac{1}{N_s}\sum_{i=1}^{N_s}\delta t_i \tag{10}$$

and N_s is the number of steps. The change in displacement after n vacancy jumps beyond the ith step is

$$\mathbf{R}_n(i)=\sum_{j=0}^{n-1}\delta\mathbf{r}_{i+j}. \tag{11}$$

Using Eq. (11) in Eq. (8) we obtain

$$f_n=1+\frac{2}{n}\sum_{j=0}^{n-1}\sum_{j'>j}^{n-1} g(j,j'), \tag{12}$$

where

$$g(j,j')=\frac{1}{N_s}\sum_i \delta\mathbf{r}_{i+j}\cdot\delta\mathbf{r}_{i+j'}. \tag{13}$$

If $N_s\gg n$ then $g(j,j')$ is a function of $(j-j')$, i.e.,

$$g(j,j')=g(0,j-j'). \tag{14}$$

Equation (14) reduces Eq. (12) to the form

$$f_n = 1 + \frac{2}{n} \sum_{j=1}^{n-1} (n-1) g(0, j). \quad (15)$$

The quantity $g(0, j)$ is the autocorrelation function for the vacancy jump displacements. Equation (15) shows that the vacancy diffusional correlation factor is a linear function of the autocorrelation function.

IV. RESULTS

In Figs. 1(a), 1(b), and 1(c) we plot the vacancy diffusional correlation factor for temperatures at about 110%, 90%, and 70% of the critical temperature ($T_c = V/0.88$).[23] Results are presented for three order parameters: disorder ($\eta = 0.0$), partial order ($\eta = 0.5$), and full order ($\eta = 1.0$). We performed the simulations using three different numbers of random seeds: 16, 64, and 128. As expected, the vacancy diffusional correlation factor decreased as the order parameter increased. However, the results from varying the number of seeds were so similar that we present only one representative example for each temperature and order parameter (solid curve). In using 4, 8, 16, and 32 test configurations (microstructures) to compute the average correlation functions, we found that the variation in the results decreased with the number of test configurations. We therefore attributed the small difference in the curves for different domain sizes to statistical fluctuations. The results for homogenous ordering of a single domain were significantly different (dashed curve) from the results of the random seed method. The vacancy diffusional correlation function decreased with the absence of domains. This effect increased in strength for alloys with larger order parameters.

In Figs. 2(a) and 2(b) we plot the vacancy diffusional correlation factor at 128 jumps, $f(128)$, for ordering with domains (a) present and (b) absent. For a given temperature, the decrease in $f(128)$ with increasing order parameter was approximately linear. A comparison of plots (a) and (b) shows that the vacancy diffusional correlation factor was smaller when domains were absent than when domains were present. The largest difference between the two cases occurred when the alloy was highly ordered.

We studied the effect of vacancy-solute interactions by including repulsive A-V and attractive B-V interactions. We choose the vacancy-solute interaction strengths to be $V_{VA} = -V_{VB} = 2.0$, and ran simulations at about 90% of the critical temperature. An oscillation in the vacancy diffusional correlation function was observed that had a period of 2 jumps (see Fig. 3). The oscillation was present in all cases when the microstructure had imperfect order. The oscillation disappeared, however, when the microstructure was perfectly ordered ($\eta = 1.0$) and had no domains. This oscillation behavior was also observed without vacancy-solute interactions when the temperatures was below (1/2) T_c.

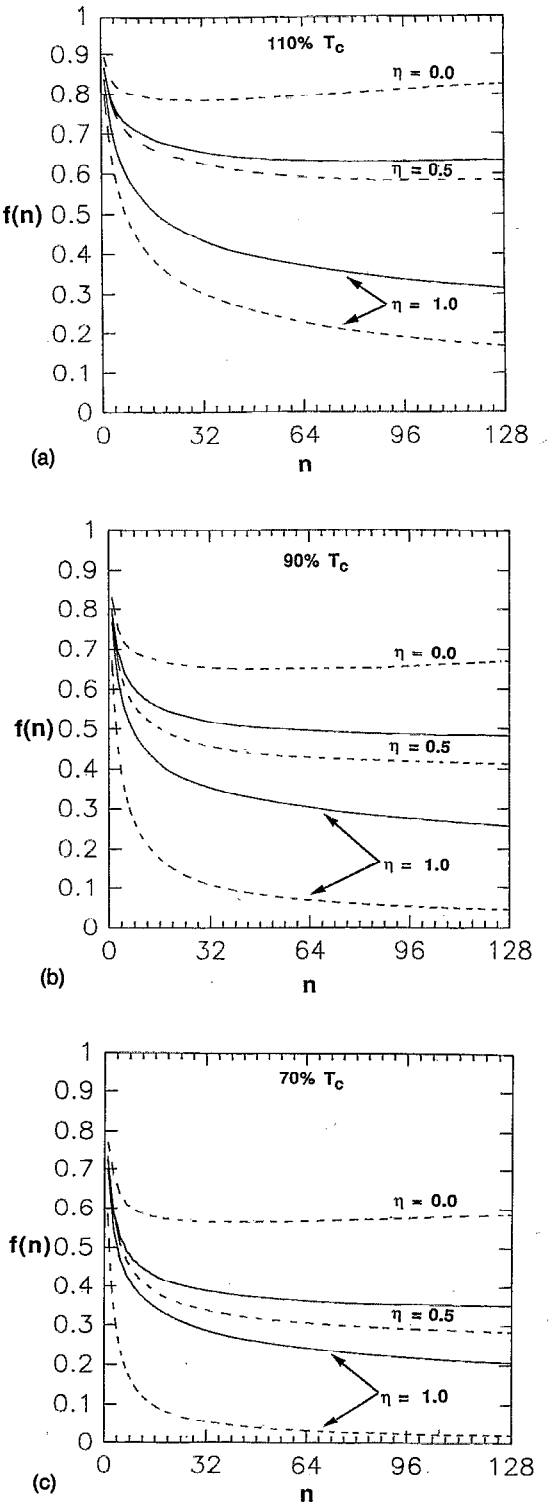

FIG. 1. Vacancy diffusional correlation factors for equiatomic square lattices with disorder ($\eta = 0.0$), partial order ($\eta = 0.5$), and perfect order ($\eta = 1.0$) for homogenous order (dashed) and with domains present (solid). The composition is 0.5 and the temperatures are (a) 110%T_c, (b) 90%T_c, and (c) 70%T_c.

V. DISCUSSION

A. Validity of the correlation factor

A single number for a diffusional correlation factor is useful in a nonequilibrium alloy if the microstructure does

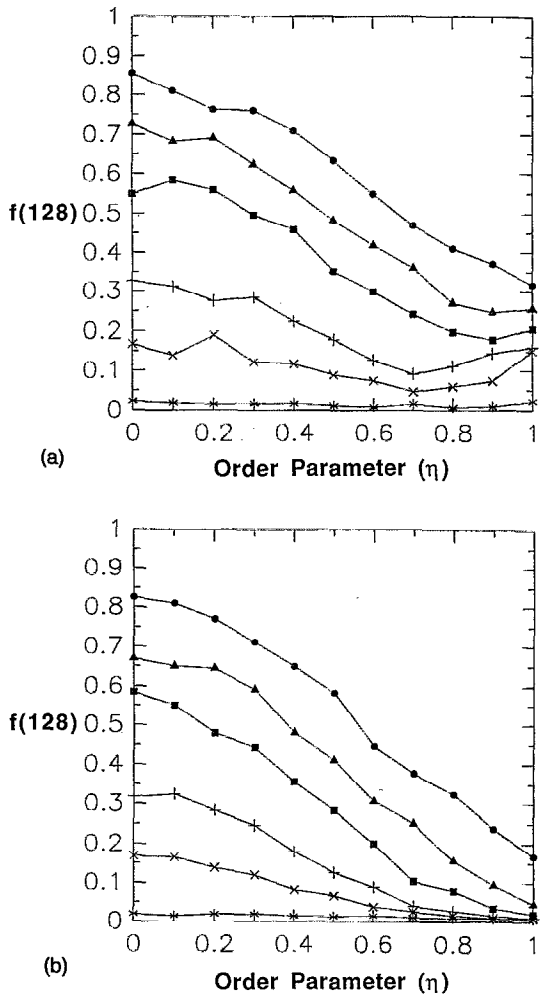

FIG. 2. Vacancy diffusional correlation factors, $f(128)$, for ordered 2-D square lattices (a) with domains present, and (b) for homogenous ordering at $110\%T_c$ (circle) $90\%T_c$ (triangle), $80\%T_c$ (square), $55\%T_c$ (plus), $45\%T_c$ (cross), and $22\%T_c$ (star).

not change significantly when the correlation factor is being measured. This can be checked as follows. Figure 4 presents diffusional correlation factors calculated with Eq. (15), assuming that $g(0, j)$ is dependent on $g(0,1)$ and j as:

$$g(0, j)=g(0,1)^j, \tag{16}$$

where $g(0,1)$ is a constant. Equation (16) is valid if all jumps occur with the same correlation to their previous jump, as is expected for homogeneous alloys in thermodynamic equilibrium, for example. Four curves for $f(n)$ are presented in Fig. 4 for rather different values of $g(0,1)$. [We confirmed that the values of $f(128)$ have converged to within the accuracy of the graph.] The shapes of $f(n)$ are similar in Figs. 1 and 4, although the convergence in the nonequilibrium alloys is slower. Most relevant is the slope of $f(n)$ for $n>64$. For the equilibrium curves in Fig. 4, the slope of $f(n)$ is essentially zero in the range $64<n<128$; the correlation factor has practically converged. This is not quite so for the nonequilibrium alloys, however, which often show a distinctly positive or negative slope for

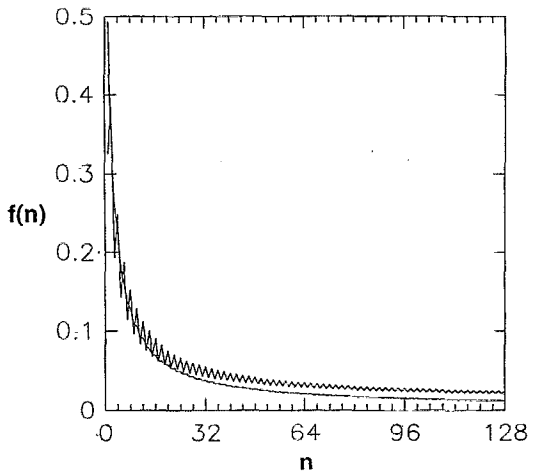

FIG. 3. Vacancy diffusional correlation factors for equiatomic square lattice at a temperature $110\%T_c$, with strong solute-vacancy interactions for disorder (upper curve) and perfect homogenous order (lower curve).

$n>64$. The origin of this slope is related to the homogeneity of the lattice. Near the starting point of the vacancy, there is a change in the state of order, and this region grows as the vacancy diffuses according to Eq. (7). The relaxation of the lattice is greatest when the alloy is furthest from thermodynamic equilibrium, as is the case for the fully ordered alloy ($\nu=1.0$) at a temperature of $1.1T_c$. The slope of $f(n)$ for $n>64$ is directly related to whether the alloy is undergoing an ordering or a disordering transformation during the measurement of the correlation factor. For example, the fully ordered alloys ($\nu=1.0$) are disordering at all three temperatures, although less so at $T=0.7T_c$. As disorder develops, the vacancy mobility decreases as more local traps for vacancies become available.[4,20–22] The opposite trend is found for the fully disordered alloy ($\nu=0.0$), where the slope is slightly positive for $n>64$. For the nonequilibrium alloys, we observed that these slopes diminished for $n>128$, but never became

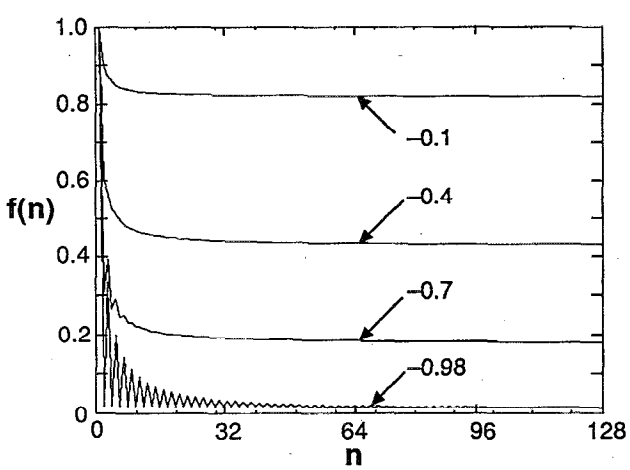

FIG. 4. Diffusional correlation factors calculated with Eqs. (15) and (16) for different values of $g(0,1)$ given as labels of the curves.

exactly zero. Good convergence was found for alloys at temperatures where their state of order was nearly that of thermodynamic equilibrium, however. The most rigorous vacancy correlation factors reported here are for highly ordered alloys at low temperatures. On the other hand, some of the other vacancy diffusional correlation factors are perhaps best regarded as semi-quantitative, since the ensemble average of $g(j, j+1)$ changes slowly with j as the alloy evolves.

B. Domains

The difference in the vacancy correlation factors for alloys that are homogenously ordered, and alloys that have domains, arises because the local environments surrounding the vacancy are different. When domains are present, the MCS shows that the vacancy motion is mostly along the domain boundaries and that the boundaries move slowly compared to the vacancy. When domains are not present, the MCS shows that vacancy motion is more correlated since an antisite atom tends to exchange with a vacancy. Therefore, the correlation factor for ordering in an alloy without domains is suppressed with respect to the correlation factor for ordering in an alloy with domains.

C. Independence of domain size

The reason why the vacancy correlation function depends on the intradomain order parameter but not the domain size can be understood in the following way. Since vacancies tend to move along the domain boundaries, the correlation function is influenced by two factors. The first is the correlation along the boundary. The intradomain order parameter strongly affects the correlation factor because it determines the local environment along the domain boundary. The second is the geometry of the domain boundary. Suppose the vacancy motion is restricted to the domain boundary. The domain boundary prevents the vacancies from moving from point to point in a straight line. The extra distance traveled leads to a decrease in the correlation factor. The ratio of this extra distance to the straight line distance is independent of domain size; so if the vacancy motion is only along the domain boundaries, the correlation function will be independent of the domain size. At any finite temperature there will always be some vacancy motion away from the domain boundary, however the motion along the domain boundary often dominates. When this is the case the correlation factor is nearly independent of the domain size.

This result can also be understood as a consequence of scaling invariance. Microstructures for different seed density will differ only in scaling and therefore will have the same orientational distribution of antiphase domain boundaries. Hence, the time will scale with the distance traveled. This argument is independent of geometrical dimension, so the independence of correlation factor on domain size is also expected for vacancy diffusion in 3 dimensions.

The independence of the vacancy diffusional correlation factor on domain size suggests that analytical theories of diffusional kinetics, which ignore the effects of domain boundaries, can be corrected in a straightforward way by multiplying their vacancy diffusional correlation factor by a constant obtained from Fig. 2(b).

D. Oscillations

Oscillations in $f(n)$ are typical of highly correlated diffusional jumps. In the extreme case when $g(0,1)=-1$, Eq. (16) shows that $g(0, n)=-1$ for n odd, and $g(0, n)=+1$ for n even. In this extreme case where each jump reverses the direction of the previous one, Eqs. (15) and (16) predict that $f(n)=0$ for all even values of n, and $f(n)=1/n$ for all odd values of n. Figure 4, for a homogeneous alloy in equilibrium, shows such oscillations in $f(n)$ with a period of two jumps when $g(0,1)=-0.98$. The inclusion of vacancy-solute interactions produced oscillations in the correlation function. Oscillations were also observed at low temperatures below $(1/2)T_c$ without vacancy-solute interactions. The oscillations arise from pair trapping, i.e., the repetitive back and forth motion of the vacancy between two adjacent sites. When pair trapping dominates, the vacancy is at its original position for even numbers of vacancy jumps and is one site away for odd jumps. This leads to an oscillation in the correlation function. The oscillation was observed when domains were present and for alloys without domains. The observed oscillations in Fig. 3 did not correspond to a completely trapped vacancy; however, we observed that the oscillation height decayed at a rate portional to $1/n$.

VI. CONCLUSION

We used Monte Carlo simulations to obtain correlation factors for vacancy diffusion in ordered alloys having different domain sizes, different states of order, and different temperatures. Since temperature determines the equilibrium state of order, the correlation factors so determined were not always characteristic of an alloy in thermodynamic equilibrium, but these correlation factors are usually useful for short time scales. Values of f as low as 0.01 were found for well-ordered alloys at low temperatures, and were explained in terms of vacancy trapping at antiphase boundaries and in small regions within the domains.

Our domain morphologies were scale-invariant, and we found that the vacancy diffusional correlation factor was independent of the domain size. This simplification permitted us to present our measurements in two groups: one for alloys with domains and one for alloys without domains.

ACKNOWLEDGMENTS

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